SOME ADDITION REACTIONS OF POLYBUTADIENE

BY

KENNETH GEORGE CLARKE

B.A., University of Buffalo, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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SOME ADDITION REACTIONS OF POLYBUTADIENE

Introduction

There has long been a need for a rubber which is both flexible at low temperatures and resistant to the action of oils and solvents. Polybutadiene is the best of the synthetic elastomers with regard to low temperature flexibility; however, its oil resistance is poor (1).

Early attempts to improve oil resistance involved the compounding of rubbers with hydrophilic substances (2).

The copolymerization of butadiene with polar monomers such as acrylonitrile has yielded polymers whose solvent resistance is increased but whose low temperature flexibility is generally decreased (1).

An alternate method of introducing polar groups into polybutadiene utilizes the polyolefinic structure of the chain. The addition of olefin reagents containing polar groups to a portion of the double bonds of polybutadiene should cause the polarity of the polymer to be increased. This increased polarity would be expected to impart greater oil resistance to the polymer (3).

The purpose of this research is to study addition reactions of this type and to ascertain the effect of various polar groups on the oil resistance and low temperature properties of polybutadiene modified in this manner.

Discussion Of Results

The addition to polybutadiene of thiols containing polar groups has been carried out in dioxane solution in the presence of free radical initiators. Hydroxyl, carboxyl, thiolacetyl, and nitrile groups have been incorporated into the polymers by this procedure. Substituted thiols containing hydroxyl, carboxyl, and thiolacetyl are readily available; however, for the incorporation of nitrile groups into polybutadiene by this

method, β-mercaptopropionitrile was synthesized and characterized.

It was found that exclusion of oxygen was essential since oxygen caused the polybutadiene to gel.

The addition product of thiosorbitol and polybutadiene, corresponding to attack of 1.2% of the double bonds, was shown to have improved oil resistance and improved low temperature flexibility, although its stress-strain characteristics were inferior to those of polybutadiene.

These addition reactions proceed in acid emulsion in the case of those thiols which are relatively insoluble in water. It was not possible to effect the addition of water soluble thiols to polybutadiene in emulsion media.

Thiocyanogen was added to polybutadiene in solution and yielded polymers whose solubility decreased as the amount of thiocyanogen added was increased.

The other olefin reagents employed in this work, sodium bisulfite, nitrosyl chloride, nitrogen trioxide, nitrogen trichloride, propionitrile-halogen mixture, and acrylonitrile, yielded polymers which were, in most cases, insoluble. They generally contained the characteristic element of the reagent added.

From the results obtained, it is obvious that the most applicable procedure for this method of incorporating polar groups into polybutadiene is the addition of substituted thiols. Addition products of polybutadiene and each of the substituted thiols investigated (thiosorbitol, mercaptoethanol, thioglycolic acid, and β-mercaptopropionitrile), in which 2-5% of the double bonds have been saturated by the addition reaction, are being prepared and evaluated as low temperature, oil resistant rubbers.

BIBLIOGRAPHY

1. Office of Rubber Reserve, private communications.

2. K. Ishiguro, Rubber Chem. & Technol., **6**, 278 (1933).

3. G. Salomon and G. J. Van Amerongen, J. Polymer Sci., **2**, 355 (1947).

VITA

Kenneth George Clarke was born August 22, 1927 in Buffalo, New York. After graduation from Buffalo Technical High School in 1945, he enlisted in the U. S. Navy. He attended the University of Buffalo and received the degree of Bachelor of Arts, with honors, from that institution in June, 1949. He began his graduate work at the University of Illinois in September, 1949 and held a half-time teaching assistantship for two semesters. From June, 1950 until June, 1952 he held a research assistantship on the Government Synthetic Rubber Program.